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APPARATUS AND METHOD FOR REMOVING COMPOUNDS FROM A SOLUTION
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- (56) Prior Art Documents
EP 460339
US 3988486
- (57) Claim

1. An apparatus for removing at least one predetermined component from a solution, including:

means for holding the solution, having a first inlet and a first outlet;

a reverse osmosis unit having a second inlet coupled to said first outlet and further having a second outlet and a third outlet;

means for driving the solution through said reverse osmosis unit for producing a retentate at said second outlet and a raw permeate at said third outlet;

a treatment column having a fourth outlet and having a third inlet coupled to said third outlet for conveying the solution therethrough for producing a purified permeate, with at least a portion of the predetermined component removed, at said fourth outlet;

means connected to said fourth outlet and to said third outlet for combining the entire purified permeate with the retentate to produce a treated solution.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

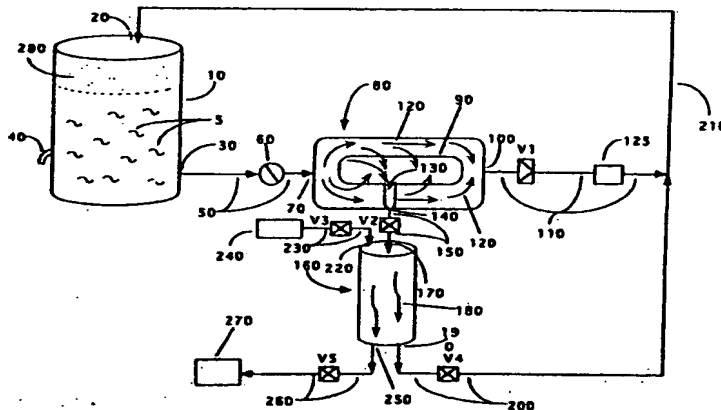
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| (51) International Patent Classification ⁵ : B01D 61/02, C12G 3/08 B01D 61/58 | | A1 | (11) International Publication Number: WO 93/23151 (43) International Publication Date: 25 November 1993 (25.11.93) |
| (21) International Application Number: PCT/US93/04197 (22) International Filing Date: 4 May 1993 (04.05.93) (30) Priority data: 07/880,659 8 May 1992 (08.05.92) US (71)(72) Applicant and Inventor: SMITH, Clark, Robert [US/ US]; 3601 Palo Verde, Napa, CA 94558 (US). (74) Agents: RAINEY, Matthew, C. et al.; Flehr, Hohbach, Test, Albritton & Herbert, 4 Embarcadero Center, Suite 3400, San Francisco, CA 94111-4187 (US). | | (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report. | |

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(54) Title: APPARATUS AND METHOD FOR REMOVING COMPOUNDS FROM A SOLUTION

(57) Abstract

Method and apparatus for the treatment of fluids, particularly wine, to remove unwanted substances. The wine is first treated in a reverse osmosis treatment unit, generating a retentate and a raw permeate. The membrane for the reverse osmosis unit is selected to pass in the permeate the unwanted substances, which in the case of wine may be volatile acidity (ethyl acetate and acetic acid). The raw permeate is then subjected to a treatment column. In the case of volatile acidity, this is an anion exchange column, which removes the acetic acid from the permeate by anion exchange and removes the ethyl acetate by base hydrolysis. This produces a purified permeate, which is depleted in volatile acidity (which is passed



through with the raw permeate), but contains other components desirable for the wine. The purified permeate is then recombined with the retentate from the reverse osmosis column, and the result is wine with the volatile acidity and little else removed. This wine may be recirculated through the system to remove yet more of the volatile acidity. The method may also be applied to the removal of acetaldehyde, in which case a distillation column is used instead of the anion exchange column, and the distillation residue constitutes the purified permeate which is recombined with the retentate from the reverse osmosis column. An embodiment utilizing a high-energy distillation column may be used to separate out alcohol and water, and then add either the alcohol or the water back to the reverse osmosis retentate, thus producing either a higher alcohol or a lower alcohol beverage, respectively.

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APPARATUS AND METHOD FOR
REMOVING COMPOUNDS FROM A SOLUTION

Background of the Invention

The present invention is directed to the removal of unwanted
5 compounds from liquids, and in particular to a recirculative
treatment process and apparatus for removing undesirable
components from wine.

It is a persistent problem in the production of wine that
certain compounds are generated in intolerable
10 concentrations, among which are ethyl acetate, acetic acid
and acetaldehyde. These compounds appear naturally in wine,
but are regarded as spoilage components because they so
alter the flavor and aroma of the wine.

It is possible to remove certain undesirable components in
15 juices by reverse osmosis treatment, but this also removes
important flavor and aroma components, resulting in a change
in the nature of the wine in addition to volume loss and
concentration effects. For instance, in U.S. Patent No.
4,401,678 to Beaumont, a process for removing methyl
20 anthranilate (which occurs in high concentration in *Vitus
labrusca* grapes) from grape juice by means of reverse
osmosis treatment is discussed. The portion of the juice
which passes through the reverse osmosis membrane,
containing methyl anthranilate and other volatile esters as
25 well as sugars and acids, is discarded, and the retentate is
diluted with water to compensate for the higher

concentration due to the reverse osmosis treatment. While this process does remove at least some of the undesirable components, it also removes many desirable components, so that the resulting juice is not suitable for making standard
5 wines from *Vitus vinifera* grapes, i.e. classic wine grapes. In certain areas, such as California, the addition of water also renders the juice illegal for the production of standard wine.

There are other processes presently used for removing
10 organic components from a fluid. For instance, in U.S. Patent No. 4,643,902 to Lawhon et al. (particularly applicable to orange and grapefruit juice), ultrafiltration is used to isolate spoilage enzymes in a retentate, with the remainder of the juice in a permeate. The enzymes are
15 deactivated, and the permeate and retentate may then be recombined. The permeate may be subjected to a reverse osmosis (R.O.) treatment to concentrate the juice before recombination with the ultrafiltration retentate. After R.O. treatment and before recombination, the juice (i.e. R.O.
20 retentate) may further be treated to deacidify it, such as by the use of an ion-exchange column. This produces a concentrate which is eventually rediluted (perhaps with the R.O. permeate, consisting of water) to reconstitute the juice.

25 This process would be deleterious in the production of high quality wine or any juice where the impact on the flavors and aromas is to be minimized, because anion exchange of the retentate removes both the undesirable components and components which are essential to the quality and value of
30 the product.

Another approach to the removal of undesirable components from a fluid is discussed in the U.S. Patent No. 4,808,287 to Hark, which uses R.O. treatment to produce ultrapure water. However, this disclosure is directed to the opposite
35 of a problem solved by the present invention; it has as

goals removing the components in the retentate (which are impurities), and keeping the entirety of the permeate.

There is thus a need for a process which can both selectively remove the undesirable components from a wine or juice and at the same time avoid concentration effects and minimize (1) the removal of components which provide aesthetic appeal, and (2) reduction in volume of the final product.

Summary of the Invention

10 The invention involves a two-stage treatment of wine or other fluid. In the first stage, the wine is subjected to R.O. treatment to remove the ethyl acetate and acetic acid (collectively referred to as "volatile acidity", or V.A.) from it. The permeate (containing the V.A.) is retained, and is itself passed through an anion exchange column. The anion exchange column provides high-pH conditions which hydrolyze ethyl acetate to ethanol and acetic acid, and the positively-charged column adsorbs substantially all of the acetate. The acetate comes both directly from the wine, passing through with the permeate, and from ester cleavage.

This selectively removes substantially all of the V.A. from the permeate, after which it is recombined with the retentate from the R.O. unit. This replaces the desirable components back into the main bulk of the wine, and the recombined wine is passed through the system again. In each pass, an additional amount of V.A. is removed, while removal of desired flavors and aromas is minimized.

This overcomes the problem of the prior approach of treating the wine merely by a reverse osmosis process. It solves a problem different from that solved in the Beaumont patent, which was directed only to the removal of certain components, and not to the retention of others.

- In an alternative embodiment, the invention may also be used to remove acetaldehyde from wine, which is responsible for characteristics of sherries, and is thus desirable in those wines but not in standard table wines. Unless one specifically wants to make sherry, acetaldehyde is regarded as a spoilage component. In order to remove it, the R.O. membrane is selected for the appropriate characteristics, and the treatment column may be a low-temperature distillation column instead of an anion exchange column.
- 10 Another embodiment uses a high-energy distillation column to remove alcohol from the permeate before returning it to the retentate. Still another embodiment involves discarding water from the bottom of the distillation column, and recombining the ethanol from the distillation column with
15 the R.O. retentate, resulting in intensified flavors and alcohol in wine made from underripe fruit.

Brief Description of the Drawings

Figure 1 shows an apparatus for implementing the method of treating fluids according to the invention.

- 20 Figure 2 shows an alternative to the apparatus of Figure 1.

Description of the Preferred Embodiments

- Although the present invention has a number of applications, the following discussion is primarily in terms of its use in the removal of undesirable components from wine. However,
25 the inventive concept can be used in general to remove components from wine which may have value in another setting, and as will be discussed can even be used to selectively increase or decrease the concentration of particular components, such as ethanol.

- 30 The apparatus for carrying this out is shown in Figure 1. The method for the use of this apparatus will first be

described below, followed by details as to specific implementation in the case of treating wine for volatile acidity (ethyl acetate or acetic acid) and acetaldehyde.

The Basic Procedure

- 5 Wine 5 is stored a tank 10 having an inlet 20, an outlet 30, and a tap 40. A pipe 50 connects the outlet 30 via a pump 60 to the inlet 70 of a conventional reverse osmosis (R.O.) treatment unit 80.

10 The pump 60 develops the high pressures necessary to effect the reverse osmosis treatment, and for this purpose a back-pressure valve V1 is used at the downstream side of the R.O. unit 80. Valve V1 is adjustable to create the proper operating pressure for the R.O. unit.

15 A typical R.O. unit may run at, for example, 450-500 psi, so once the pump 60 is running, the valve V1 will be closed off to the extent necessary to achieve this pressure. (Different units may require different pressures.) Standard minimum and maximum pressure cut-off safety switches may also be provided in the pipe 50, downstream of the pump 60.

20 The R.O. unit 80 includes a conventional R.O. membrane 90, and has an outlet 100 coupled to a pipe 110, into which a retentate 120 of the R.O. unit 80 is conveyed. The retentate includes most of the original constituent compounds of the solution.

25 It will be appreciated that the membrane 90 is conventional, and is selected on the basis of characteristics (e.g, the molecular weights which the membrane will pass) which are designed to remove particular, predetermined undesirable substances-in this case, ethyl acetate and acetic acid.

30 Some membranes may be more efficient than others at removal of a particular component, and some empirical testing will generally be necessary to find the most efficient. In the

present application, a MILLIPORE R25A membrane has been found to be effective at removing V.A.

The retentate is inevitably heated by the pumping process, due to the high pressures. While this may not be of concern in the treatment of some fluids, for wine it is a problem because it unacceptably changes the characteristics of the beverage. Therefore, a heat exchanger 125 is coupled into the flow of the pipe 110 to bring the temperature down to a desired level, in this case preferably no more than about 70° F. Conventional R.O. units actually operate more efficiently at higher temperatures, so there is a balance to be achieved between efficiency of R.O. treatment and minimizing unwanted effects of heat on the solution.

The R.O. unit 80 also produces a raw permeate 130, which passes through an outlet 140 into a pipe 150. The raw permeate 130 is then conveyed through a treatment column 160 via an inlet 170, which in the embodiment for removing volatile acidity (V.A.) from wine comprises an anion exchange column. In a manner discussed in detail below, the column 160 removes some (and preferably substantially all) of the V.A. or other undesirable component from the wine, and produces a purified permeate 180 which passes through an outlet 190 and into a pipe 200.

The pipes 190 and 110 are preferably coupled into a single pipe 210, so that the purified permeate 180 is mixed with the retentate 120 from the R.O. unit 80. The product may at this point be drawn off at tap 40, or may be recirculated in the system to remove yet more of the V.A.

In order to prevent oxidation of the wine, a nitrogen cap 280 is created on the wine tank, and the entire system is hermetically sealed.

The Action of the Column

The column 160 at the beginning of the procedure is in a condition which optimizes the removal of the components in question. With V.A., it has been found that an initial pH of about 11 for the column is effective. Thus, the column is initially charged in a conventional fashion (such as by flushing with a 4% KOH solution) to this pH, and is then rinsed, if desired, to remove potassium. The flushing may be forward-flushing (from top to bottom) or back-flushing (from bottom to top). Several dead volumes (i.e. volumes of the resin column) are passed through.

The resin in the charged column includes R-NH₂ groups covalently bonded to the resin of the anion exchange column. These groups form R-NH₃⁺ groups, due to interaction with the low-pH raw permeate (which in this case includes acetic acid, which is partially ionized and present as acetate). The NH₃⁺ binds electrostatically with the acetate, thereby preventing it from passing through as part of the purified permeate. This results in the gradual lowering of the pH of the column.

As the raw permeate passes through the anion exchange column, ethyl acetate does not interact with the R-NH₃⁺ groups in the same manner as the acetate does. However, the column is at a basic pH (as noted above, it is initially charged to about pH 11). The column becomes more and more acidic as a greater amount of acetate is extracted of the raw permeate as discussed above. Thus, a pH gradient develops, with lower-pH resin (more acidic) at the top, and higher-pH resin (more basic) at the bottom. As the ethyl acetate approaches the regions of high pH, it is base hydrolyzed, resulting in ethanol and acetic acid. The acetic acid is then ionized and adsorbed by the column in the manner described above.

The purified permeate is thus reduced in both ethyl acetate and acetic acid. Since the R.O. unit does not remove all of the acetate and ethyl acetate from the retentate (65% is more typical), the purified permeate and the retentate are
5 mixed back into the tank of wine. The remixed solution is run through the process repeatedly, until a desired low level of the unwanted substances is achieved.

The resin in the column 160 is conventional, and for a given application, one familiar with anion exchange columns will
10 be able to select a suitable resin. For the present embodiment, it has been found that a PURALITE™ A-107 resin is effective for removing V.A.

Recharging the Column

After a period of use, the anion exchange column 160 will be
15 depleted, i.e. will be in such an acidic condition that it will not be very effective for removing the V.A. While this is a matter of degree, in the present embodiment the column is considered depleted when the pH of the liquid exiting at the bottom of the column is about 5. It may also be
20 determined as a function of the amount of V.A. or other undesired substance remaining in the permeate exiting the column.

When the column is depleted, it must be recharged. This is a standard procedure in the use of such columns, and is
25 basically carried out as follows. As shown in Figure 1, the pipe 150 includes an in-line valve V2, and the column 160 includes another inlet 220 into which is coupled a pipe 230 connected to a container 240 of KOH solution. A valve V3 is positioned in line with the pipe 230.

30 A valve V4 is positioned in line with the pipe 200. The column 160 includes another outlet 250 coupled to a pipe 260, which includes an in-line discharge valve V5. The outlet of the pipe 260 leads to a discharge container 270.

To recharge the column 160, the pump 60 is turned off and valves V1 and V2 are closed, and then valve V3 is opened to allow the KOH solution to flow (by gravity or pumping) from container 240 into the column 160. This is done until about
5 one bed volume of fluid has flowed into the column, and hence one bed volume of wine has been forced out of the column and into the pipe 200.

Before the KOH is passed through the column 160, an initial rinse with purified water may be used.

10 Valve V4 is then closed, and the discharge valve V5 is opened. The KOH (or water) now passes into the discharge container 270. This is essentially a potassium acetate solution, in the case of removing V.A. from wine.

The KOH solution is passed through the column 160 until it
15 again reaches pH 11. It may then also be flushed (such as with purified, deoxygenated water), to remove free potassium ions, and it is ready to use as described before.

The above process is carried out in a manner to prevent the introduction of oxygen.

20 The procedure is carried out for as long as necessary to deplete the level of the undesired substance to a tolerable level. This is necessarily a matter of judgment, but in the case of wine, the threshold concentrations of various substances, including ethyl acetate and acetic acid, are
25 well known within certain ranges.

Other Embodiments and Applications

In order to remove acetaldehyde from wine, the R.O. membrane 90 is selected to pass acetaldehyde in the raw permeate 130. In this case, the column 160 is preferably a low-energy
30 distillation column, and the purified permeate 180 comprises the distillation residue. Thus, the anion exchange column

is not used in this embodiment. The distillation process is well known, and is adapted for the removal of acetaldehyde, including recirculating the distillate (for multiple distillations), if desired.

- 5 Application of the above-discussed method and apparatus to other fluids may also be made. In each case, the R.O. membrane is selected to pass in the raw permeate the substance to be excluded. This is followed by the treatment, such as anion exchange or distillation, which is
- 10 adapted for the removal of the specific substance in question. Then follows the recombination with the retentate from the R.O. unit. The recombined fluid may be used at that point, or it may be recirculated into the system for further purification.
- 15 The treatment column 160 may alternatively be a high-energy distillation column, so that the apparatus may be used to either increase or decrease the amount of alcohols (such as ethanol) in wine or other beverages. The alcohol is separated out by distillation in a conventional fashion. If
- 20 the alcohol level is to be decreased, then the distillation residue (lower in alcohol) is taken as the purified permeate 180, and is recombined with the retentate. In this case, alcohol is considered the undesired component to be removed, although it may still be valuable for other purposes.
- 25 If the alcohol level is to be increased, then the distillate (higher in alcohol) is taken as the purified permeate 180, and is recombined with the retentate. In this case, water is considered the undesired component.

- 30 In the embodiments wherein the treatment column is a distillation column, then such an intricate flushing apparatus as that shown in Figure 1 (for embodiments where the treatment column 160 is an anion exchange column) is not needed. However, conventional methods of cleansing the distillation column should be used.

In general, the undesired component, be it an aesthetically displeasing compound, a diluent or otherwise, can be selectively targeted for removal by this method and apparatus.

- 5 Another variation on the invention is illustrated in Figure 2, wherein the numeral 300 generally designates the treatment apparatus of the invention as shown in Figure 1, other than the tank 20 and pipe 50. In this embodiment, the treated, recombined solution from tank 20 is conveyed via a
10 pipe 320 to another tank 310. If desired, it may be run through the treatment apparatus 300 again, from tank 310 to tank 20, using pipes (not separately shown) which are in a configuration opposite that of pipes 50 and 320. All of these pipes preferably include appropriate valves (not
15 separately shown) to control the flow of the fluids into and out of the appropriate tanks, and the fluids may be gravity fed or pumped as desired.

The configuration of Figure 2 is advantageous in that it conveys all of the solution 5 through the R.O. unit in a
20 single pass, which is more efficient for removing the undesired substances. The treated solution, in the reverse configuration mentioned above, again is conveyed through the R.O. unit in a single pass. This leads to higher overall efficiency and speed in removing unwanted components from
25 the solution. As in the circulative embodiment of Figure 1, the process is carried out enough times to remove as much of the unwanted components as desired.

Claims

1. An apparatus for removing at least one predetermined component from a solution, including:

means for holding the solution, having a first inlet
5 and a first outlet;

a reverse osmosis unit having a second inlet coupled to said first outlet and further having a second outlet and a third outlet;

means for driving the solution through said reverse
10 osmosis unit for producing a retentate at said second outlet and a raw permeate at said third outlet;

a treatment column having a fourth outlet and having a third inlet coupled to said third outlet for conveying the solution therethrough for producing a purified permeate,
15 with at least a portion of the predetermined component removed, at said fourth outlet;

means connected to said fourth outlet and to said third outlet for combining the entire purified permeate with the retentate to produce a treated solution.

20 2. The apparatus of claim 1, wherein said treatment column is an anion exchange column.

3. The apparatus of claim 1, wherein said treatment column is a distillation column.

4. The apparatus of claim 1, further including means for
25 passing the treated solution again through the apparatus.

5. The apparatus of claim 1, wherein:

the at least one predetermined component includes acetic acid;

said reverse osmosis unit includes a membrane
30 configured for passing at least acetic acid in said raw permeate; and

said treatment column is an anion exchange column for removing acetic acid from the raw permeate.

6. The apparatus of claim 5, wherein:

the at least one predetermined component also includes ethyl acetate;

said membrane is configured for also passing ethyl
5 acetate in said raw permeate; and

said treatment column includes means for base hydrolyzing the ethyl acetate for removing it from the raw permeate.

7. The apparatus of claim 6, wherein the base hydrolyzing
10 means comprises a region of high pH in said treatment column.

8. The apparatus of claim 1, wherein:

said reverse osmosis unit includes a membrane for passing at least the predetermined component in said raw
15 permeate; and

said treatment column is a distillation column for removing at least some of the predetermined component from the raw permeate.

9. The apparatus of claim 8, wherein:

20 said predetermined component includes acetaldehyde; and said purified permeate comprises the distillation residue from the distillation column.

10. The apparatus of claim 8, wherein:

said predetermined component includes an alcohol; and
25 said purified permeate comprises the distillation residue from the distillation column.

11. The apparatus of claim 8, wherein:

said predetermined component includes an alcohol; and said purified permeate comprises the distillate from the
30 distillation column.

12. A method for treatment of a solution to remove at least one predetermined component, including the steps of:

(1) processing the solution by reverse osmosis for producing a retentate and a raw permeate, with the raw permeate containing the predetermined component;

(2) treating the raw permeate for removing at least a portion of the predetermined component and for producing a purified permeate; and

(3) combining the retentate with the purified permeate for producing a treated solution.

13. The method of claim 11, wherein step 2 comprises passing the raw permeate through an anion exchange column.

14. The method of claim 13, wherein the predetermined component includes acetic acid.

15. The method of claim 13, wherein:

the predetermined component includes ethyl acetate; and step 2 includes the step of base hydrolyzing the ethyl acetate.

16. The method of claim 12, wherein:

the at least one predetermined component includes acetic acid; and

step 1 is carried out such that acetic acid is at least partially removed from the retentate and is passed with the raw permeate.

17. The method of claim 12, wherein:

the at least one predetermined component includes ethyl acetate;

step 1 is carried out such that ethyl acetate is at least partially removed from the retentate and is passed with the raw permeate.

18. The method of claim 9, wherein step 2 comprises passing the raw permeate through a distillation column, and the purified permeate comprises the distillate from the distillation column.

19. The method of claim 18, wherein:

the at least one predetermined component includes acetaldehyde; and

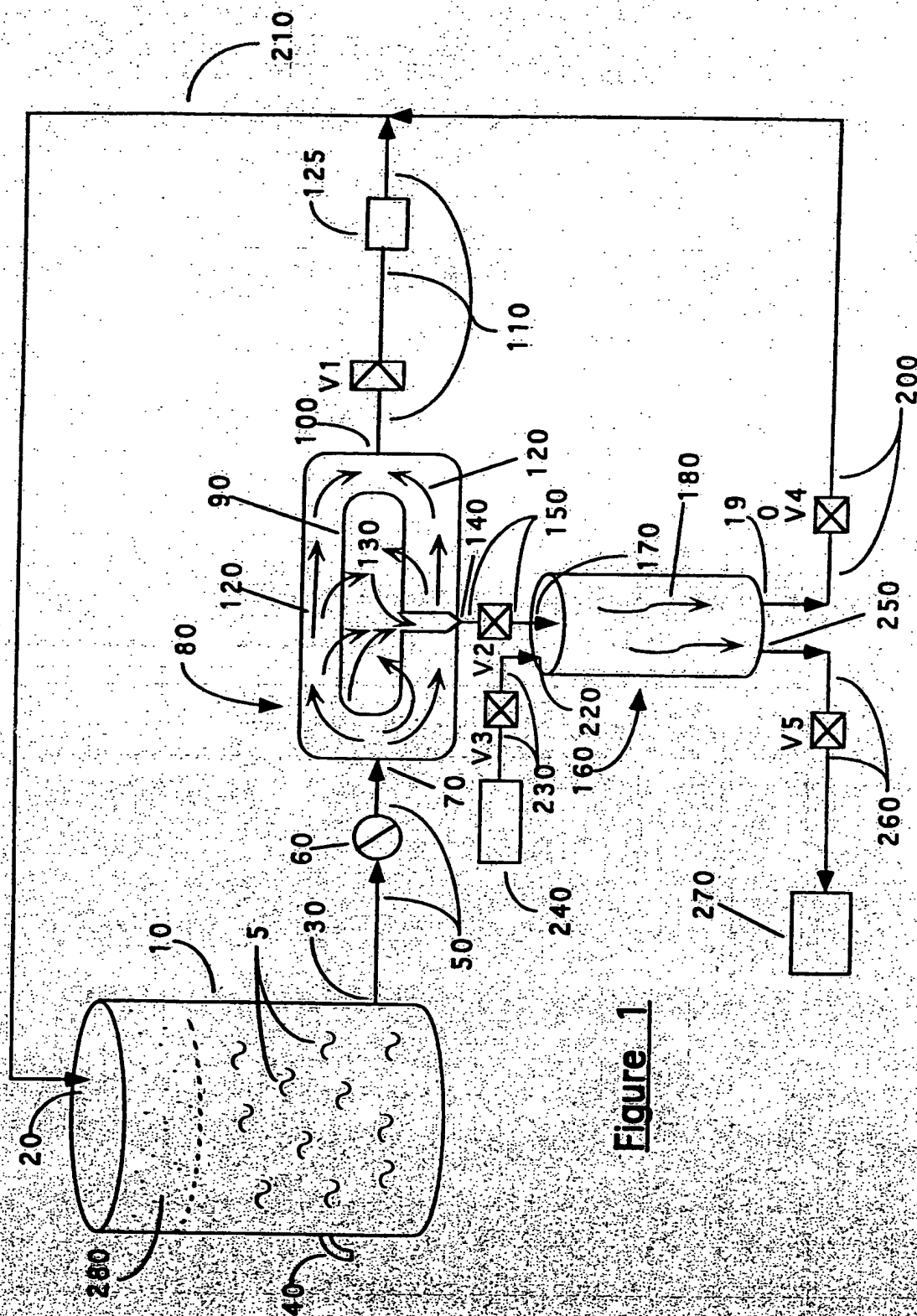
step 1 is carried out such that the acetaldehyde is
5 substantially removed from the retentate and is passed with
the permeate.

20. The method of claim 12, wherein step 2 comprises
passing the raw permeate through a distillation column for
producing a portion higher in alcohol and a portion lower in
10 alcohol.

21. The method of claim 20, wherein the purified permeate
comprises the portion lower in alcohol, for recombination
with the retentate for producing a low-alcohol treated
solution.

15 22. The method of claim 20, wherein the purified permeate
comprises the portion higher in alcohol, for recombination
with the retentate for producing a high-alcohol treated
solution.

23. The method of claim 12, further including the step of:
20 (4) carrying out steps 1, 2 and 3 on the treated solution,
for removing more of the predetermined component from the
solution.

**Figure 1**

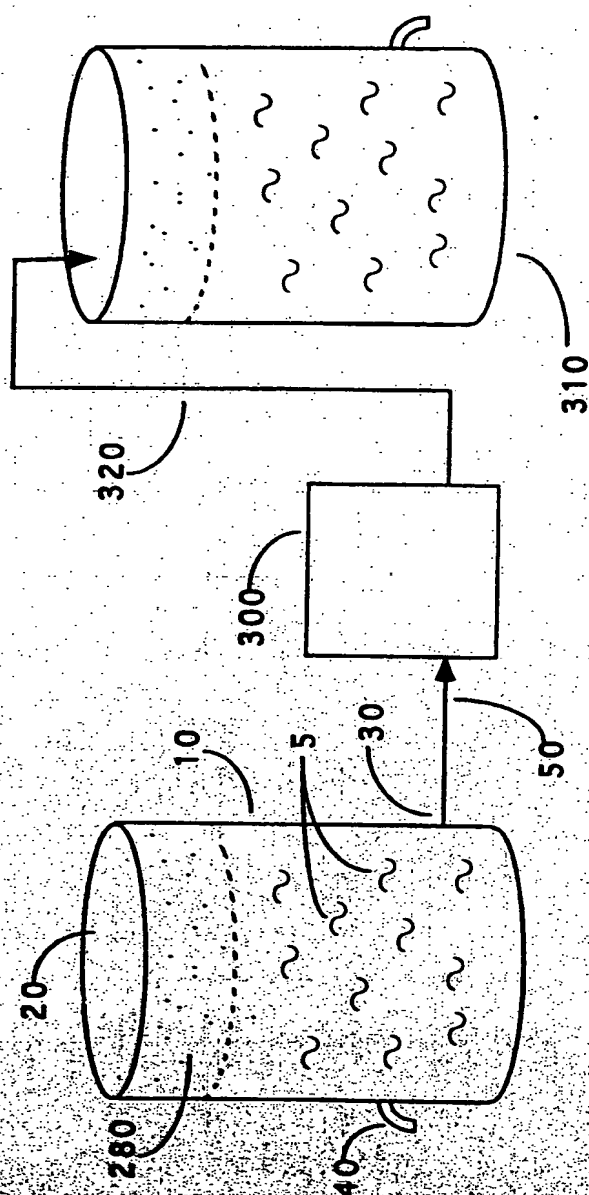


Figure 2

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/04197

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 B01D61/02; C12G3/08; B01D61/58

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl. 5

B01D ; C12G

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

| Category ¹⁰ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
|------------------------|--|-------------------------------------|
| A | EP,A,0 162 240 (HENKELL & CO.) 27 November 1985 see the whole document | 1 |
| A | EP,A,0 089 893 (UNION DE BRASSERIES) 28 September 1983 see the whole document | 1 |
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| A | EP,A,0 460 339 (MEMBRANE PRODUCTS KIRYAT WEITZMANN LTD.) 11 December 1991 see the whole document | 1 |
| A | DD,A,204 493 (Z. SZIRANY ET AL.) 30 November 1983 | |

* Special categories of cited documents :¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

23 JULY 1993

Date of Mailing of this International Search Report

11. 08. 93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

DEVISME F.R.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9304197
SA 74102

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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23/07/93

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| EP-A-0460339 | 11-12-91 | AU-B- 624250 | 04-06-92 |
| | | AU-A- 5706490 | 19-12-91 |
| DD-A-204493 | | None | |

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